Transition-metal Complexes of Crown Ether Benzodithiolenes

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Three new dithiolene ligands have been synthesised, two of which have the novel feature of a crown ether ring attached directly to the benzene ring of an aryl dithiolene. Complexes with transition metals have been prepared and their ^1H, ^{13}C NMR, UV/VIS and electrochemical properties recorded. The information obtained appears to reflect variations in the degree of delocalisation in the metallodithiolene ring within the series of complex types.

The binding of 'guest' alkali-metal cations to the crown ether moiety of appropriate derivatives has been shown to be manifest through perturbation of the physical properties of the 'host' compound. Typically, perturbations have been reported in the electrochemistry,[1] optical properties,[2] acidity[3] and NMR spectra[4] of such systems. Recently, much effort has been directed towards the maximisation of such perturbations, stimulated by the possible application of such reagents for the assay of alkali-metal cations in solution, particularly in biomedical situations. Furthermore, the majority of this work has focused on the electrochemical perturbations produced by alkali-metal cations.[5]

The strategy behind the development of such electrochemical 'sensor' reagents has been to locate a redox-active transition-metal centre in close proximity to a macrocycle appended to one, or more, of the ligands bound to the transition-metal centre. The resulting electrochemical perturbations seem to be largest when the 'through space' distance between the redox centre and the cation-binding site is minimised.[6] However, it has also been demonstrated that significant perturbations result in cases where the cation-binding site is linked to the redox centre through a delocalised bonding system.[7] In this vein, Green *et al.*[8] have recently exploited the π delocalisation of transition-metal dithiolene complexes to relay the electronic effects of cation binding to the redox centre. We have followed a similar course by synthesising crown ether benzodithiolene ligands and using them to prepare a series of transition-metal complexes.[9]

This paper describes the synthesis and characterisation of three new dithiolene ligands and several of their complexes with transition-metal centres. The perturbation of the physical properties of these transition-metal complexes which occur upon addition of alkali-metal cations will form the basis of a subsequent publication.[10]

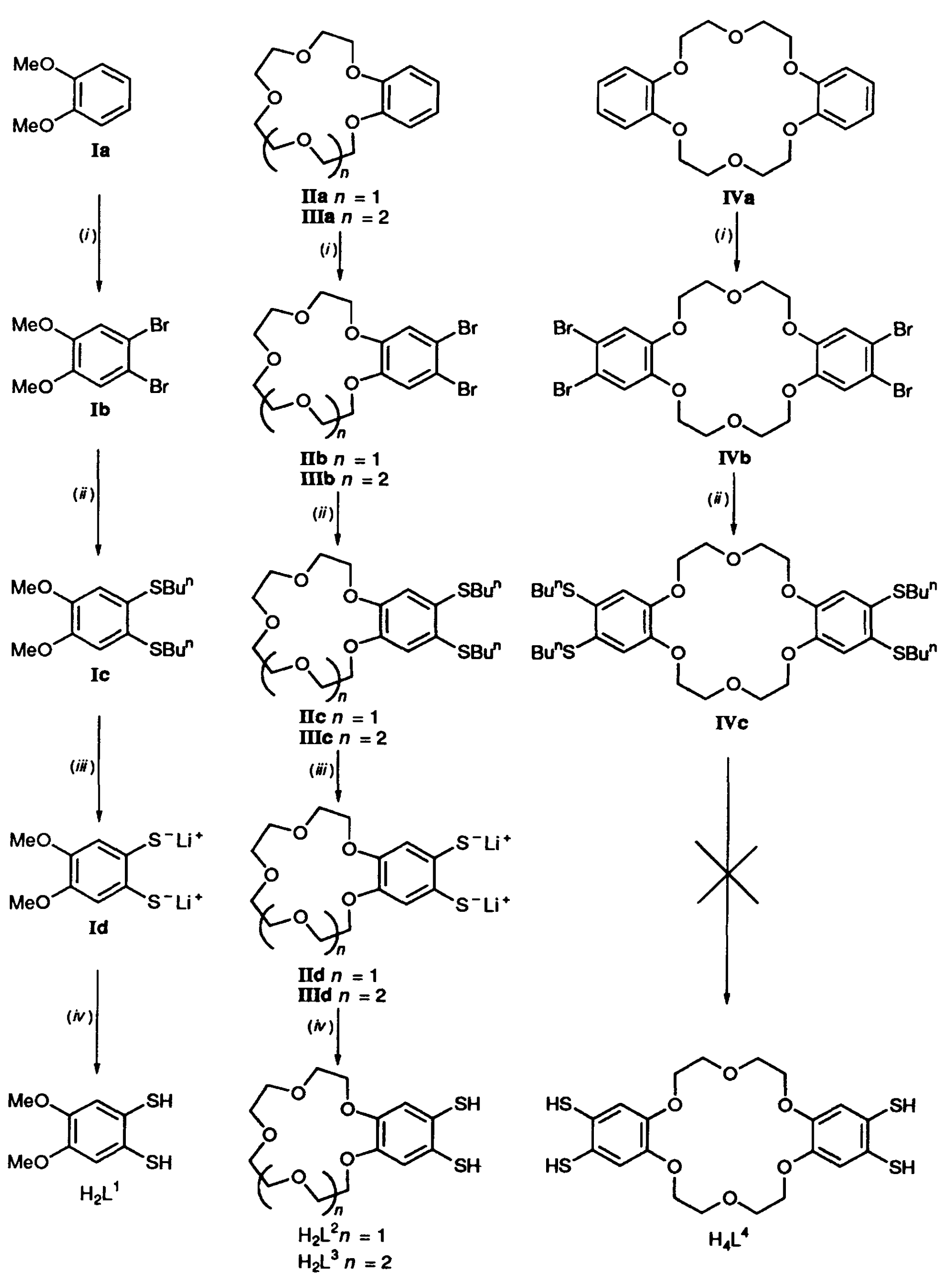
Results and Discussion

Initially, it was our objective to synthesise the range of dithiolene ligands H_2L^1, H_2L^2, H_2L^3 and H_4L^4 (Scheme 1); ultimately, H_4L^4 was not isolated even though several precursors were characterised. The synthetic route outlined was employed in all cases and parallels the standard synthesis of benzene-1,2-dithiol.[11,12] Following the previously reported dibromination of catechol,[13] it was found that veratrole (1,2-dimethoxybenzene **Ia**), benzo-15-crown-5 (2,3,5,6,8,9,11,12-octahydro-1,4,7,10,13-benzopentaoxacyclopentadecine **IIa**), benzo-18-crown-6 (2,3,5,6,8,9,11,12,14,15-decahydro-1,4,7,10,13,16-benzohexaoxacyclooctadecine **IIIa**) and dibenzo-18-crown-6 (6,7,9,10,17,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecine **IVa**) could be brominated smoothly in acetic acid solution to yield the corresponding dibromo-derivatives, **Ib**–**IVb**, both rings being dibrominated in the case of dibenzo-18-crown-6.[14] 1,2-Dibromo-4,5-dimethoxybenzene **Ib** was usually produced by prior dibromination of catechol,[13] followed by methylation of the hydroxy groups with dimethyl sulfate in concentrated, aqueous sodium hydroxide. All compounds were characterised by ^{13}C and ^1H NMR, mass spectral and microanalytical results, except where specified. These data are included in the Experimental section. As has been reported previously (for **IVb**[14]), all crown ether dibromo-derivatives were produced, initially, as molecular bromine complexes by reaction with an excess of bromine in solution. The excess of bromine could be removed by treatment with aqueous sodium metabisulfite ($NaHSO_3$), or by dissolution of the crude dibromo-products in acetone with concomitant evolution of HBr, followed by removal of the volatiles at reduced pressure.

The *o*-dibromo-compounds **Ib**–**IVb** were successfully converted into the corresponding *o*-bis(*n*-butylthio)ethers **Ic**–**IVc** by reaction with copper(I) butanethiolate in yields of 50–70%.[11] The products were usually isolated as dark oils, though solids were separated in the case of **Ic** and **IIc** which have been fully characterised; **IIIc** and **IVc** have been identified on the basis of ^1H NMR and mass spectra and **IVc** was produced, in low yield, as part of a mixture (other constituents included species where replacement of all four bromine atoms by the Bu^nS groups was incomplete even after a 24 h reflux). Further attempts to produce the bis(dithiol) H_4L^4 were abandoned at this stage.

The *n*-butyl groups of the series of compounds **Ic**–**IIIc** were cleaved by treatment with alkali metals in liquid ammonia to yield the crude dithiolate salts, from which the dithiols, H_2L^1–H_2L^3, were liberated by treatment with aqueous, concentrated hydrochloric acid.[12] Lithium proved to be most effective in the liquid ammonia reduction stage. Attempts to purify and characterise fully the dithiols were unsuccessful due to their sensitivity to oxidation. Compounds H_2L^1–H_2L^3 were formed, initially, as green oils which darkened on exposure to the atmosphere. Prolonged attempts to isolate a pure sample of H_2L^1, working under anaerobic conditions, led only to the isolation of a material indicated by its mass spectrum to be a dimeric species presumably linked by two persulfide bridges. The ^{13}C, ^1H NMR and mass spectra recorded for crude samples of H_2L^1–H_2L^3 clearly showed dominant signals consistent with the presence of the required free dithiols as major constituents of the reaction mixture. Consequently, the crude reaction products were used directly in the syntheses of transition-metal complexes.

In view of the wide range of known metal–dithiolene complexes,[15,16] it seemed important to select a few representative types which would allow investigation of the factors important



Scheme 1 (*i*) $MeCO_2H$, Br_2, *ca.* 90% yield; (*ii*) $CuSBu^n$, quinoline–pyridine (3 : 1 v/v), 60–70% yield; (*iii*) Li, $NH_3(l)$, thf; (*iv*) HCl (aq)

to the effectiveness of the crown ether dithiolene complexes as alkali-metal cation-sensitive reagents. For instance, the effect of changing the number of ion-binding sites on the sensitivity of the complexes to alkali-metal cations can be investigated by preparing metal complexes with one, two or three of the crown ether ligands. Also, the importance of the degree of delocalisation in the metallodithiolene ring can be assessed by measuring the cation sensitivity of a series of complexes which, according to NMR data, exhibit differing degrees of delocalisation. The complexes synthesised in the course of this study, along with relevant analytical and spectroscopic data, are included in Table 1. However, analytical data have not been included where reproducible results were not obtained. The formulation of these complexes was based upon the spectroscopic evidence discussed below. The isolation of stoichiometrically pure materials proved difficult, particularly for complexes of the crown ether ligands H_2L^2 and H_2L^3. Inclusion of solvent and/or adventitious binding of cations could be a source of contamination and would affect the analytical data. However, the complexes **1**–**17** were all readily identifed by the gross similarity of their spectroscopic and electrochemical data to each other and to those of established and corresponding dithiolene complexes. All of the complexes were air-stable, both in solution and in the solid state, over the time-scale of their preparation and during measurement of their physical properties. Long-term storage was usually under dinitrogen as a precautionary measure.

The tris(dithiolene) complexes **1**–**5** were prepared by reaction of the appropriate dithiol with either $MoCl_5$ or WCl_6, according to previous methods.[17] The molybdenum complexes were isolated as dark red-brown solids of which **1** was recrystallised from hexane-layered dichloromethane solutions giving red-green dichroic crystals which were subjected to X-ray analysis. Owing to problems of disorder, the structure could not be fully refined, though the MoS_6 core was located.[18] The tungsten compounds **4** and **5** were isolated as dark green solids. The $[Ni(dithiolene)_2]^-$ complexes **6**–**8** were synthesised *via* procedures established for the analogous compound $[NR_4][Ni(tdt)_2]$ (tdt = toluene-3,4-dithiolate),[19] the dipotassium salt of the dithiol ligand being added to a solution of $NiCl_2{\cdot}6H_2O$ in

Table 1 Analytical and spectroscopic data for complexes **1**–**17**

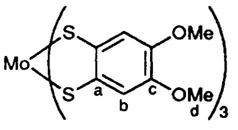
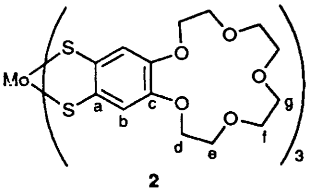
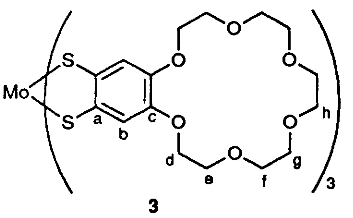
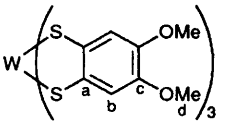
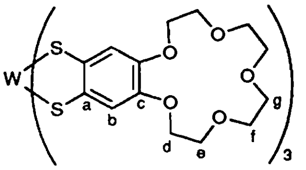
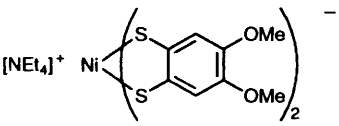
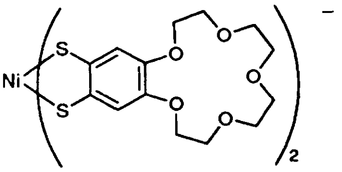
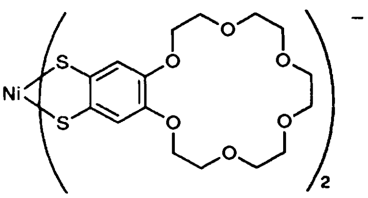
			Analysis (%)[b]				
	Colour	*m/z*[a]	C	H	S	M, *etc.*	NMR data[c]
 **1**	Dark red	698(60)	39.3 (41.4)	3.5 (3.5)	25.3 (27.6)	Mo 12.5 (13.8)	^{1}H: 7.60 (s, 6 H_b), 3.95 (s, 18 H_d) ^{13}C: 158.2 (C_a), 149.6 (C_c), 110.0 (C_b), 54.4 (C_d)
 **2**	Red-brown	1088(20)	45.4 (46.4)	5.2 (5.0)	15.9 (17.7)	Mo 7.9 (8.8)	^{1}H: 7.55 (s, 6 H_b), 4.17 (br s, 12 H_d), 3.90 (br s, 12 H_e), 3.72 (br s, 24 $H_{f,g}$) ^{13}C: 158.3 (C_a), 149.2 (C_c), 111.0 (C_b), 71.2 (C_d), 70.2 (C_e), 69.0 (C_f), 68.6 (C_g)
 **3**	Red-brown	—	*d*	*d*	*d*	*d*	^{1}H: 7.52 (s, 6 H_b), 4.3–4.0 (br s, 12 H_d), 4.0–3.85 (br s, 12 H_e), 3.85–3.50 (br s, 36 $H_{f,g,h}$) ^{13}C: 158.1 (C_a), 149.3 (C_c), 110.9 (C_b), 70.6 (C_d), 70.5 (C_e), 69.2 (C_f), 68.9 (C_g), 68.6 (C_h)
 **4**	Dark green	784(90)	36.2 (36.8)	3.1 (3.1)	23.3 (24.5)	W 22.2 (23.4)	^{1}H: 7.55 (s, 6 H_b), 3.94 (s, 18 H_d) ^{13}C: 155.1 (C_a), 149.4 (C_c), 110.7 (C_b), 56.2 (C_d)
 **5**	Dark green	1174(75)	41.7 (42.9)	4.7 (4.6)	15.2 (16.4)	W 13.3 (15.7)	^{1}H: 7.56 (br s, 6 H_b), 4.16 (br s, 12 H_d), 3.91 (br s, 12 H_e), 3.74 (br s, 24 $H_{f,g}$) ^{13}C: 149.4 (C_c), 113.7 (C_b), 71.1 (C_d), 70.1 (C_e), 69.0 (C_f), 68.7 (C_g), C_a not seen
 **6**	Green	458(80)	49.7 (48.9)	6.3 (6.1)	19.6 (21.7)	Ni 11.6 (10.0) N 2.5 (2.4)	*g* = 2.063[e]
 **7**	Green	718(75)	*d*	*d*	*d*	*d*	*g* = 2.062[e]
 **8**	Yellow-green	—	*d*	*d*	*d*	*d*	*g* = 2.068[e]

Table 1 (*continued*)

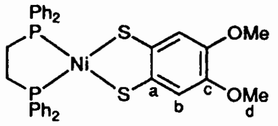
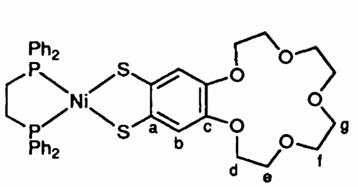
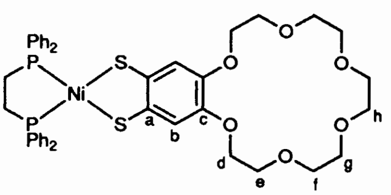
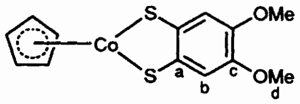
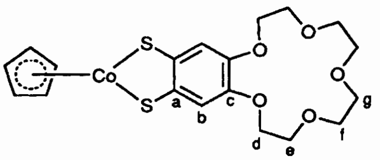
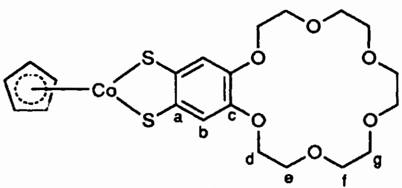
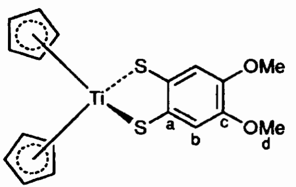
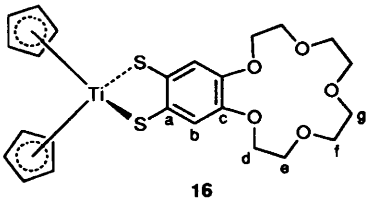
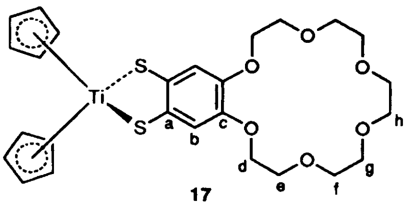
	Colour	*m*/*z*[a]	Analysis (%)[b]				NMR data[c]
			C	H	S	M, *etc.*	
 **9**	Purple	656(90)	61.1 (62.1)	4.85 (4.90)	9.4 (9.7)	Ni 8.5 (8.9) P 8.7 (9.4)	^{1}H: 7.86 (4 lines, 8 H, Ph), 7.48 (5 lines, 12 H, Ph), 6.96 (s, 2 H$_b$), 3.73 (s, 6 H$_d$), 2.36 [d, *J*(HH) = 16.5, 4 H, CH$_2$ of dppe] ^{13}C: 145.1 (C$_c$), 140.4 [t, *J*(CP) = 9.3, C$_a$], 133.7 [t, *J*(CP) = 5.3, C$_{o/m}$ of Ph], 131.3 (C$_p$ of Ph), 129.8 [t, *J*(CP) = 22.5, C$_i$ of Ph], 128.7 [t, *J*(CP) = 4.7, C$_{o/m}$ of Ph], 110.3 (C$_b$), 55.9 (C$_d$), 27.6 [t, *J*(CP) = 23.5, CH$_2$ of dppe][f]
 **10**	Purple	786(100)	60.1 (61.0)	5.3 (5.4)	8.0 (8.1)	Ni 7.65 (7.50) P 7.6 (7.9)	^{1}H: 7.80 (br s, 8 H, Ph), 7.43 (br d, 12 H, Ph), 6.92 (s, 2 H$_b$), 3.96 (br s, 4 H$_d$), 3.80 (br s, 4 H$_e$), 3.70 (br s, 8 H$_{f,g}$), 2.35 [d, *J*(HH) = 16.5, 4 H, CH$_2$ of dppe] ^{13}C: 145.0 (C$_c$), 141.5 [t, *J*(CP) = 9.3, C$_a$], 133.8 [t, *J*(CP) = 5.3 Hz, C$_{o/m}$ of Ph], 131.4 (C$_p$ of Ph), 129.8 [t, *J*(CP) = 22.3, C$_i$ of Ph], 128.9 [t, *J*(CP) = 4.7, C$_{o/m}$ of Ph), 113.3 (C$_b$), 71.1 (C$_d$), 70.6 (C$_e$), 69.8 (C$_f$), 69.3 (C$_g$), 27.6 [t, *J*(CP) = 23.5, CH$_2$ of dppe]
 **11**	Purple	831(85)	[d]	[d]	[d]	[d]	^{1}H: 7.75 (br d, 20 H, Ph), 6.92 (s, 2 H$_b$), 4.0 (br s, 4 H$_d$), 3.80 (br s, 4 H$_e$), 3.66 (br d, 12 H$_{f,g,h}$), 2.34 [br d, *J*(HH) = 16.5, 4 H, CH$_2$ of dppe] ^{13}C: 144.5 (C$_c$), 141.4 [t, *J*(CP) = 9.5, C$_a$], 133.6 [t, *J*(CP) = 5.1, C$_{o/m}$ of Ph], 131.3 (C$_p$ of Ph), 129.7 [t, *J*(CP) = 22.6, C$_i$ of Ph], 128.9 [t, *J*(CP) = 4.5, C$_{o/m}$ of Ph], 112.8 (C$_b$), 70.6 (C$_d$), 70.5 (C$_{e,f}$), 69.6 (C$_g$), 68.8 (C$_h$), 27.5 [t, *J*(CP) = 23.4, CH$_2$ of dppe]
 **12**	Blue-purple	324(100)	[d]	[d]	[d]	[d]	^{1}H: 7.51 (s, 2 H$_b$), 5.36 (s, 5 H, C$_5$H$_5$), 3.84 (s, 6 H$_d$) ^{13}C: 155.8 (C$_a$), 147.0 (C$_c$), 111.0 (C$_b$), 79.2 (C$_5$H$_5$), 56.0 (C$_d$)
 **13**	Blue	454(70)	[d]	[d]	[d]	[d]	^{1}H: 7.50 (s, 2 H$_b$), 5.35 (s, 5 H, C$_5$H$_5$), 4.1–3.4 (br m, 16 H, H$_{d,e,f,g}$) ^{13}C: 155.9 (C$_a$), 146.7 (C$_c$), 112.9 (C$_b$), 79.2 (C$_5$H$_5$), 71.1 (C$_d$), 70.2 (C$_e$), 69.2 (C$_f$), 68.5 (C$_g$)
 **14**	Blue	498(90)	[d]	[d]	[d]	[d]	^{1}H: 7.49 (s, 2 H$_b$), 5.36 (s, 5 H, C$_5$H$_5$), 4.11 (m, 4 H$_d$), 3.95–3.70 (m, 4 H$_e$), 3.70–3.50 (m, 12 H$_{f,g,h}$) ^{13}C: 155.9 (C$_a$), 146.6 (C$_c$), 112.8 (C$_b$), 79.3 (C$_5$H$_5$), 70.9 (C$_d$), 70.8 (C$_e$), 70.7 (C$_f$), 69.3 (C$_g$), 68.8 (C$_h$)
 **15**	Green	378(50)	51.3 (57.1)	4.4 (4.8)	17.0 (16.9)	Ti 11.2 (12.7)	^{1}H: 6.99 (s, 2 H$_b$), 6.10 (vbr s, 5 H, C$_5$H$_5$), 5.64 (vbr s, 5 H, C$_5$H$_5$),[d] 3.85 (s, 6 H$_d$) ^{13}C: 148.5 (C$_{a/c}$), 147.6 (C$_{a/c}$), 112.3 (vbr, C$_5$H$_5$), 111.0 (C$_b$), 110.0 (vbr, C$_5$H$_5$),[d] 55.7 (C$_d$)

Table 1 (*continued*)

			Analysis (%)[b]				
	Colour	m/z[a]	C	H	S	M, *etc.*	NMR data[c]
 **16**	Green	508(100)	52.5 (56.7)	5.3 (5.5)	11.1 (12.6)	Ti 8.6 (9.4)	^{1}H: 7.00 (s, 2 H_b), 6.20 (vbr s, 5 H, C_5H_5), 5.68 (vbr s, 5 H, C_5H_5),[d] 4.16 (m, 4 H_d), 3.92 (m, 4 H_e), 3.80 (d, 8 $H_{f,g}$) ^{13}C: 149.1 ($C_{a/c}$), 147.9 ($C_{a/c}$), 114.1 (C_b), 112.8 (vbr, C_5H_5), 110.1 (vbr, C_5H_5),[d] 71.2 (C_d), 70.4 (C_e), 69.5 (C_f), 68.7 (C_g)
 **17**	Green	552(95)	*d*	*d*	*d*	*d*	^{1}H: 6.95 (s, 2 H_b), 6.15 (vbr s, 5 H, C_5H_5), 5.64 (vbr s, 5 H, C_5H_5),[d] 4.11 (br s, 4 H_d), 3.86 (br s, 4 H_e), 3.67 (br d, 12 $H_{f,g,h}$) ^{13}C: 148.9 ($C_{a/c}$), 147.3 ($C_{a/c}$), 113.7 (C_b), 112.6 (vbr, C_5H_5), 110.3 (vbr, C_5H_5),[d] 70.6 (C_d), 70.5 (C_e), 70.4 (C_f), 69.2 (C_g), 69.0 (C_h)

[a] FAB (positive ion except for **6–8**), percentage abundance in parentheses. [b] Calculated values in parentheses. [c] At room temperature, in $CDCl_3$, at 300 (^{1}H) and 75 MHz (^{13}C); *J* in Hz. [d] See text. [e] Paramagnetic species, solution *g* value. [f] ^{31}P-{^{1}H} NMR (32.4 MHz): δ 58.4 (s) (reference H_3PO_4).

Table 2 Selected ^{13}C and ^{1}H NMR data for the dithiols H_2L^1–H_2L^3 and their transition-metal complexes

Compound	δ(C_a)[a]	δ(H_b)[b]
H_2L^1	122.0	6.83
1	158.2	7.55
4	155.1	7.60
9	140.4	6.96
12	155.8	7.51
15	148.1[c]	6.99
H_2L^2	122.7	6.90
2	158.3	7.55
5	*d*	7.56
10	141.5	6.92
13	155.9	7.50
16	148.5[c]	7.00
H_2L^3	*d*	6.80[e]
3	158.1	7.52
11	141.4	6.92
14	155.9	7.49
17	148.1[c]	6.95

[a] Chemical shift of carbons bonded to sulfur (C_a), recorded at room temperature (r.t.), in $CDCl_3$, at 75 MHz. [b] Chemical shift of aryl protons (H_b) recorded at r.t., in $CDCl_3$, at 300 MHz unless otherwise specified. [c] Average chemical shift of both substituted aryl carbon atoms (C_a and C_c) since signals indistinguishable. [d] Data not available. [e] Recorded at r.t., in $CDCl_3$, 80 MHz.

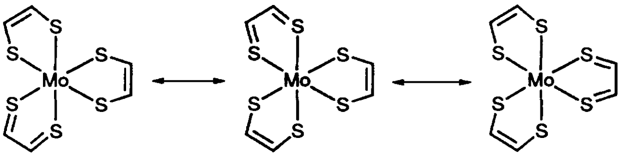


Fig. 1 Resonance structure representation of a [Mo^{IV}(dithiolene)$_3$]

absolute ethanol, giving a red-brown solution. Salt **6** was precipitated as a green solid by addition of [NEt_4]Br. The species **7** and **8** could be isolated only as yellow-green oils and the identity of the cations is unclear as several different salts had been added in an attempt to produce a solid, crystalline product. The diphosphine nickel dithiolene complexes **9–11** were produced by reaction of the disodium salt of the appropriate dithiol with [Ni(dppe)Cl_2][20] (dppe = $Ph_2PCH_2CH_2PPh_2$) in dichloromethane solution, followed by recrystallisation of the crude product from dichloromethane to give shiny, purple needles. Complex **11** proved more difficult to recrystallise, elemental analysis revealing that it was not obtained as a pure material. Complexes **12–14** were synthesised by reaction of the dipotassium salts of the corresponding dithiols with [Co(η^5-C_5H_5)(CO)I_2] in dichloromethane solution, following established procedures, and isolated as dark blue solids.[21] The titanocene derivatives **15–17** were synthesised by adding the free dithiols to dichloromethane solutions of [Ti(η^5-C_5H_5)$_2Cl_2$] in the presence of triethylamine,[22] the products being isolated as green solids.

The ^{13}C and ^{1}H NMR properties of the three aryl dithiolene ligands H_2L^1–H_2L^3 were strongly dependent upon the type of transition-metal complex in which they were incorporated. This is most apparent from the chemical shifts of the carbon atoms (C_a) to which a sulfur is attached. Similar behaviour is also seen in the chemical shifts of the aryl protons (H_b). These data, together with relevant data for the free dithiols, are summarised in Table 2. In the case of ligand H_2L^1, for instance, the chemical shift of C_a ranges from δ 122.0 for the free dithiol to δ 158.2 for the molybdenum tris(dithiolene) complex **1**. This large downfield shift upon complexation can be attributed to the formation of a delocalised metallodithiolene unit. Several molecular orbital treatments of such systems[23,24] have indicated the molybdenum oxidation state to be considerably less than its formal value of VI, with some 'dithioketonic' character in the dithiolene ligands. For instance, a molybdenum oxidation state of IV could be described by the resonance structures of Fig. 1, each with a single 'dithioketonic' ligand.[24] Such delocalisation in metallodithiolene rings is consistent with the NMR properties of complexes of ethylenedithiol[24] and styrenedithiol[25] and also with the Friedel–Crafts-type reactivity of [Ni($S_2C_2H_2$)$_2$] which indicates a degree of aromaticity.[15] The higher-field resonances recorded for C_a are thought to indicate complexes in which the dithiolene ligand is more 'dithiolate' in character, as is suggested for the diphosphine nickel dithiolene complexes **9–11**. The latter are formulated as nickel(II) complexes of the form [{(diphosphine)Ni}$^{2+}${dithiolene}$^{2-}$].[26] The data in Table 2 suggest that the degree of aromaticity decreases in the order: [M(dithiolene)$_3$] (M = Mo or W) **1–5** > [Co(dithiolene)(η^5-C_5H_5)] **12–14** > [Ti(dithiolene)(η^5-C_5H_5)] **15–17** > [Ni(dithiolene)(dppe)] **9–11**. The relative order of the titanocene derivatives **15–17** and the corresponding cyclopentadienylcobalt complexes **12–14** within this series has been suggested by earlier studies of the ethylenedithiol derivatives.[27] The absence of comparable data for the paramagnetic [Ni(dithiolene)$_2$]$^-$

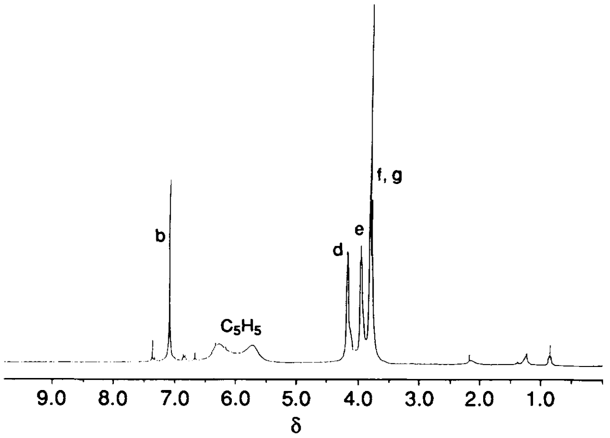


Fig. 2 The 300 MHz ^{1}H NMR spectrum of complex **16** (in $CDCl_3$)

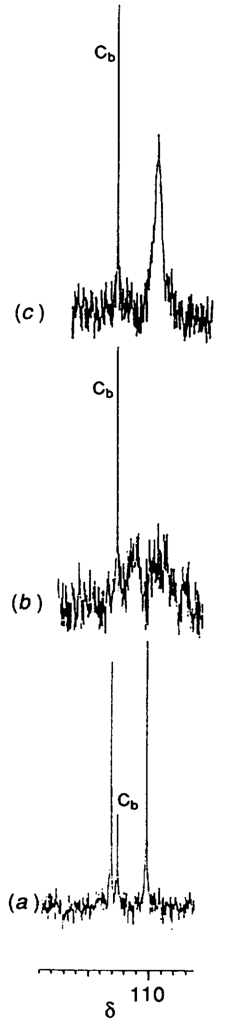


Fig. 3 The 75 MHz ^{13}C NMR spectrum of complex **16** (in $CDCl_3$) at (*a*) 223, (*b*) 295 and (*c*) 323 K

species **6–8** prevents their location within this series, though previous studies have suggested that there is considerable metal–ligand delocalisation in such anions.[28] The *g* values of the $[Ni(dithiolene)_2]^-$ systems fall within the range observed previously, $g = 2.057–2.082$.[19]

The ^{1}H NMR spectrum of the crown ether benzodithiolene complex **16** is shown in Fig. 2. This spectrum is typical of those recorded in this study with an additional feature seen for all the $[Ti(\eta^5-C_5H_5)_2]$ complexes **15–17**. Both ^{13}C and ^{1}H NMR spectra indicate that the two cyclopentadienyl rings of these complexes are inequivalent in solution at room temperature. This is illustrated by the two broad resonances in the ^{1}H NMR spectrum of **16** shown in Fig. 2. Such behaviour is consistent with a fluxional process of the type indentified previously for analogous compounds and shown schematically in Fig. 4.[29] The coalescence behaviour was studied by both ^{1}H and ^{13}C NMR spectroscopy (Fig. 3) and the free energy of activation for the process, $\Delta G^\ddagger$, was obtained using the Eyring equation (1),[30]

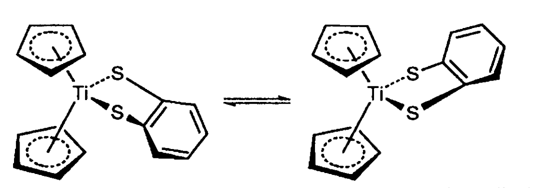


Fig. 4 Fluxional process in a dicyclopentadienyltitanium dithiolene complex (illustrated for a benzene-1,2-dithiol ligand)

Table 3 Solution UV/VIS absorption maxima for complexes **1–17**

Complex	λ/nm (ε/dm^3 mol^{-1} cm^{-1})
1	773(14 500), 477(8 000)[a]
2	777(13 400), 478(7 600)[a]
3	778(12 100), 475(6 900)[a]
4	740(28 500), 434(13 200)[a]
5	745(15 600), 434(10 500)[a]
6	995(21 500), 765(2 700), 700(sh, 1 500), 520(375), 363(15 700), 312(34 400)[b]
7	965s, 766w, 363s, 310s[b]
8	*c*
9	575(330)[b]
10	570(310)[b]
11	566(250)[b]
12	635(11 100), 288(25 000)[b]
13	634(9 800), 288(25 100)[b]
14	632(6 800), 288(19 400)[b]
15	636(3 000), 466(2 300), 305(7 000), 256(24 500)[b]
16	634(3 300), 466(2 700), 308(7 800), 259(26 200)[b]
17	*c*

[a] In CH_2Cl_2. [b] In MeCN. [c] Qualitatively similar to analogues.

$$\Delta G^\ddagger = -RT_c \ln(hk/k_b T_c) \qquad (1)$$

where T_c = coalescence temperature and $k = \pi\Delta\delta/2$,[31] with $\Delta\delta$ being the separation, in Hz, of the signals at the low-temperature limit. Values of $\Delta G^\ddagger$ for complexes **15–17** were found to lie in the range 58–63 kJ mol^{-1} similar to values measured in previous studies.[29]

The UV/VIS absorption spectra of transition-metal dithiolene complexes are intense and characteristic of the complex type[15] and greatly assisted in the identification and characterisation of the complexes reported herein. Absorption coefficient data were also used to assess the purity of materials. The absorption data are summarised in Table 3.

The homoleptic dithiolene complexes **1–8** all manifest strong absorptions in the visible region ($\varepsilon > 10\,000$ dm^3 mol^{-1} cm^{-1}) which are attributed to ligand-to-metal charge-transfer transitions.[17,32] It is interesting to compare the visible λ_{max} values with those for analogous complexes of the toluene-3,4-dithiolate (tdt) ligand. In all cases, those of the latter ligand occur at a higher energy {$[Mo(tdt)_3]$ 684 (20 900), 435 (17 400);[17] $[W(tdt)_3]$ 638 (23 400), 386 (15 700);[17] $[NEt_4][Ni(tdt)_2]$ 890 nm (16 270 dm^3 mol^{-1} cm^{-1})[32]} consistent with a greater separation between the ligand and metal orbitals for the tdt complexes as compared to the dithiolenes H_2L^1–H_2L^3. This reflects the relatively electron-rich nature of the latter ligands. The similarity in absorption positions for complexes of ligands H_2L^1–H_2L^3 shows that changing the methyl group of the veratroledithiol ligand H_2L^1 for the crown ether rings of ligands H_2L^2 and H_2L^3 has little effect on the properties of the

Table 4 Cyclic voltammetric data for complexes **1**–**8** and their toluene-3,4-dithiolate (tdt) analogues (potentials relative to a saturated calomel electrode)

Complex	E_1/V	$\Delta E_p{}^a$/mV	E_2/V	$\Delta E_p{}^a$/mV
[Mo(tdt)$_3$]^b	+0.29	70	−0.37	80
1^b	+0.03	70	−0.44	80
2^b	+0.03	90	−0.44	90
[W(tdt)$_3$]^c	+0.26	*d*	−0.55	*d*
4^e	+0.04	80	−0.56	100
5^e	+0.06	90	−0.56	100
[NEt$_4$][Ni(tdt)$_2$]^b	+0.45	100	−0.45	100
6^b	+0.22	110	−0.52	110
7^b	+0.22	110	−0.53	100
8^b	+0.18	110	−0.58	120

[a] ΔE_p for the ferrocene–ferrocenium couple under the conditions employed was *ca.* 80 mV. [b] Recorded in CH_2Cl_2, 0.2 mol dm^{-3} [NBu$_4$][BF$_4$], scan rate 200 mV s^{-1}. [c] Polarography data from ref. 17. [d] Data not available. [e] Recorded in MeCN, 0.2 mol dm^{-3} [NBu$_4$][BF$_4$], scan rate 200 mV s^{-1}.

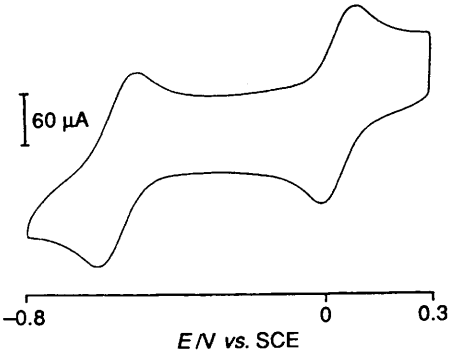


Fig. 5 Typical cyclic voltammogram of complex **5** recorded at 200 mV s^{-1}, in MeCN solution, with 0.2 mol dm^{-3} [NBu$^n{}_4$][BF$_4$] as supporting electrolyte

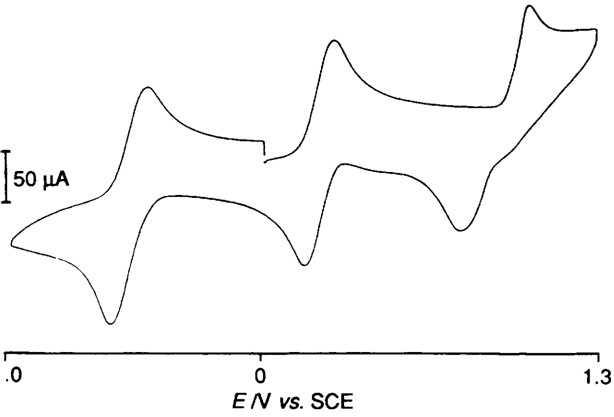


Fig. 6 Typical cyclic voltammogram of complex **6** recorded at 200 mV s^{-1}, in CH_2Cl_2 solution, with 0.2 mol dm^{-3} [NBu$^n{}_4$][BF$_4$] as supporting electrolyte

dithiolene complexes. Similar comments can be made about the visible region absorptions of complexes **12**–**17**, in that the absorption positions are almost identical across the series of ligands H_2L^1–H_2L^3 but occur at a lower energy than for their tdt analogues.[9] If absorption coefficients are taken as a measure of the extent of ligand-to-metal charge transfer, the latter decreases in the order: [Ni(dithiolene)$_2$]$^-$ **6**–**8** > [M(dithiolene)$_3$] (M = Mo and W) **1**–**5** > [Co(dithiolene)(η^5-C$_5$H$_5$)] **12**–**14** > [Ti(dithiolene)(η^5-C$_5$H$_5$)$_2$] **15**–**17** > [Ni(dithiolene)(dppe)] **9**–**11**. This order is the same as that derived from the ^{1}H and ^{13}C NMR data, reflecting decreasing delocalisation in the metallodithiolene ring and is consistent with the increasing 'dithiolate' character of the ligands from **6**–**8** to **9**–**11**.

Table 5 Cyclic voltammetric data for complexes **9**–**17** and their toluene-3,4-dithiolate (tdt) analogues (potentials relative to a saturated calomel electrode)

Complex^a	E_{red}/V	$\Delta E_p{}^b$/mV	E_{ox}/V
[Ni(tdt)(dppe)]^c	−1.03	*d*	*d*
9	−1.51	120	+0.52
10	−1.51	140	+0.56
11	−1.51	130	+0.56
[Co(tdt)(C$_5$H$_5$)]^e	−0.60	70	*d*
12	−0.66	80	+0.72
13	−0.65	80	+0.76
14	−0.65	80	+0.76
[Ti(tdt)(C$_5$H$_5$)$_2$]^e	−0.92	180	+1.05
15	−1.03	100	+0.73
16	−1.04	90	+0.73
17	−1.03	90	+0.84

[a] Recorded in MeCN, 0.2 mol dm^{-3} [NBu$_4$][BF$_4$], scan rate 200 mV s^{-1}. [b] ΔE_p for the ferrocene–ferrocenium couple under the conditions employed was *ca.* 80 mV. [c] Data from ref. 26. [d] Data not cited. [e] Ref. 33.

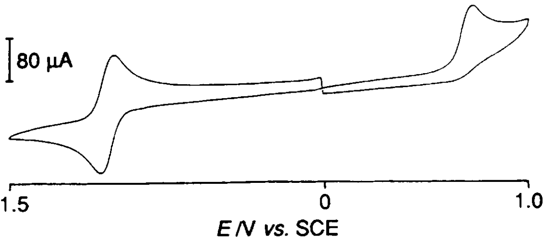


Fig. 7 Typical cyclic voltammogram of complex **16**. Details as in Fig. 6

Transition-metal dithiolene complexes are also known for their extensive redox chemistry.[15] Except in the case of **3**, where insufficient quantities precluded detailed electrochemical studies, cyclic voltammetry was used to investigate the redox properties of complexes **1**–**17**. These cyclic voltammograms were entirely consistent with the proposed formulation of the complexes. Half-wave potentials, for each reversible couple, were more cathodic in all cases than those reported for the corresponding tdt complexes,[15] in keeping with the proposed electron-rich nature of ligands H_2L^1–H_2L^3 (see above). Furthermore, the data were nearly identical for the corresponding complexes of each of the ligands H_2L^1–H_2L^3. For complexes **1**–**8** two reversible couples (E_1 and E_2) were measured in each case and the relevant data are summarised in Table 4 together with the corresponding data for the tdt analogues. Complexes **9**–**17** each display a reversible reduction feature (E_{red}) and an irreversible oxidation (E_{ox}). These data and the corresponding information for the tdt analogues are included in Table 5. Some typical cyclic voltammograms are shown in Figs. 5–7.

Cyclic voltammograms for the tris(dithiolene) complexes **1**–**5** showed two reversible reductions corresponding to the couples [M(dithiolene)$_3$]–[M(dithiolene)$_3$]$^-$ (E_1) and [M(dithiolene)$_3$]$^-$–[M(dithiolene)$_3$]$^{2-}$ (E_2).[17] Of these, the couple E_1 is more sensitive to the change of ligand. For the complex anions **6**–**8** the two reversible processes were identified as corresponding to [Ni(dithiolene)$_2$]–[Ni(dithiolene)$_2$]$^-$ (E_1) and [Ni(dithiolene)$_2$]$^-$–[Ni(dithiolene)$_2$]$^{2-}$ (E_2).[19,34] A third feature, at *ca.* 1.05 V, was observed in dichloromethane solution which was not reversible, though a related reduction wave was seen at + 0.77 V (Fig. 6). When the cyclic voltammetry of complexes **6**–**8** was performed in acetonitrile solution the oxidation E_2 became irreversible whilst E_1 was unaffected. However, an anomalously large reduction current was observed for the couple E_1 when scanned after the irreversible oxidation of E_2. This large reduction current could be due to the adsorption of a product of the oxidation since the reduction couple is normal if scanned on its own. Cyclic voltammetry of the complexes **9**–**17** (Table 5) revealed only a single, reversible process corresponding to a reduction of the neutral compound in each case.

Some of the larger deviations of the peak separations ΔE_p (in Tables 4 and 5) from the theoretical value of 59 mV reflect a departure from the criterion of true electrochemical reversibility.[35] However, in all cases, the criterion of chemical reversibility was met, the ratio of the peak currents for each couple being close to unity within experimental error. No scan-rate dependence studies were undertaken to establish the true electrochemical reversibility of the couples reported here. Couples are described as 'reversible' largely by analogy with similar systems which have been reported in the literature. It is conspicuous that the order of the measured half-wave potentials for the reversible reduction of the species **1**–**17** (most positive first) is $[Ni(dithiolene)_2]^-$ **6**–**8** > $[M(dithiolene)_3]$ (M = Mo or W) **1**–**5** > $[Co(dithiolene)(\eta^5-C_5H_5)]$ **12**–**14** > $[Ti(dithiolene)(\eta^5-C_5H_5)_2]$ **15**–**17** > $[Ni(dithiolene)(dppe)]$ **9**–**11**. This is the same order of decreasing delocalisation of the metallodithiolene ring as found in the NMR and absorption coefficient data. Also, a recent study of complexes of the type $[Co\{S_2C_2X(Y)\}(\eta^5-C_5H_5)]$ (where X and Y represent various substituents) has established a similar trend, in this case a linear relationship between the reduction potential and the ^1H and ^{13}C chemical shifts of the cyclopentadienyl ring.[36] The more negative the reduction potential, the lower are the chemical shift values. The relationship suggests that a constant fraction of the electronic effects of the substituents X and Y extends to the cyclopentadienyl ring through the dithiolene–cobalt bonding. Interestingly, complexes **12**–**14** comply with this trend since both the ^1H and ^{13}C chemical shifts of the cyclopentadienyl rings are lower than those of the tdt analogue.

Conclusion

Three, new dithiolene ligands H_2L^1–H_2L^3 have been synthesised, two of which have the novel feature of a crown ether ring attached directly to the benzene ring of an aryl dithiolene. These ligands have been used to prepare a range of transition-metal complexes. Trends in the physical properties of these complexes appear to reflect the type of chemical bonding in each species and show the new ligands to be more strongly electron donating than dithiolenes such as tdt.

Experimental

Dibenzo-18-crown-6 obtained commercially from Aldrich was used without further purification. Benzo-15-crown-5 and benzo-18-crown-6 were synthesised following the literature procedures.[37] 4,5-Dibromobenzene-1,2-diol (4,5-dibromocatechol) was prepared following literature methods,[13] as was copper(I) butanethiolate.[11] The NMR data for the ligands H_2L^1–H_2L^3 and their precursors are reported using the labelling system given for the transition-metal complexes in Table 1. The complexes were synthesised under dinitrogen using standard Schlenk-tube and vacuum-line techniques because of the air sensitivity of the free dithiols. All the products were air-stable but were usually stored under dinitrogen. Dichloromethane was dried by prolonged reflux over CaH_2, followed by distillation, for use with the highly moisture-sensitive reagents $MoCl_5$ and WCl_6.

Proton and ^{13}C NMR spectra were recorded on Varian XL300 and Bruker AC300E spectrometers (at 300 and 75 MHz, respectively) with some ^1H spectra recorded (at 80 MHz) on a Bruker AC80E machine. Spectra were referenced internally using the solvent resonance relative to $SiMe_4$ ($\delta = 0$). The EPR spectra were recorded as fluid solutions on a Varian E-4 spectrometer operating at 9.50 GHz, mass spectra on Kratos MS30 [electron impact (EI), 70 eV (*ca.* 1.12×10^{-17} J)], MS25 [chemical ionisation (CI), using ammonia] and Concept (FAB, *m*-nitrobenzyl alcohol matrix) instruments and UV/VIS spectra on a Shimadzu 260 electronic absorption spectrometer with 0.1 cm matched silica cells. Cyclic voltammetric measurements were recorded using a Princeton Applied Research model 173 potentiostat and a model 175 Universal Programmer with a vitreous carbon working electrode and a platinum secondary electrode, usually in MeCN, though CH_2Cl_2 was used for the $[Ni(dithiolene)_2]^-$ complexes for the reasons discussed in the text. All experiments used $[NBu^n{}_4][BF_4]$ as the background electrolyte (0.2 mol dm^{-3}). The electrolyte solution was 0.001 mol dm^{-3} in sample and, typically, scan rates of 200 mV s^{-1} were used. All potentials are quoted in volts relative to a saturated calomel electrode (SCE) connected to the cell *via* an appropriate bridge tube. The $[Fe(\eta^5-C_5H_5)_2]^+$–$[Fe(\eta^5-C_5H_5)_2]$ couple was measured at +0.56 and +0.43 V relative to the SCE under these conditions in CH_2Cl_2 and MeCN, respectively.

All other standard reagents were obtained commercially and used without further purification, except where specified.

Syntheses—1,2-*Dibromo*-4,5-*dimethoxybenzene* **Ib**.—4,5-Dibromocatechol (5 g, 0.019 mol) and NaOH (2.24 g, 0.056 mol) were placed in a round bottom flask (25 cm^3) and water (2 cm^3) added to the solids. The flask was warmed, with occasional agitation, for 15 min producing a dark green paste. Dimethyl sulfate (4.7 g, 5.6 cm^3, 0.037 mol) was added dropwise with concurrent agitation whilst the flask was cooled in an ice-bath. When this addition was complete, the mixture was allowed to warm to room temperature and then heated, under reflux, in an oil-bath, for 1 h. Performing these manipulations under dinitrogen was found to increase the yield slightly. After the reflux a brown sludge remained which hardened on cooling. This was extracted several times with ethyl acetate (4 × 15 cm^3). The dark red extract was washed with water (4 × 15 cm^3) and dried over $MgSO_4$. After removal of the solvent, the crude material was recrystallised from a minimum volume of dry hexane to give pale orange needles. Yield *ca.* 60%. The course of the reaction was followed satisfactorily by TLC, both the product and the starting material giving distinctive, dark blue spots on silica gel plates when sprayed with a solution of cerium(IV) sulfate in sulfuric acid and warmed on a hotplate (Found: C, 33.1; H, 2.7; Br, 51.6. $C_8H_8Br_2O$ requires C, 32.5; H, 2.7; Br, 54.0%); *m/z* (EI) 296 (100%, M^+, ^{79}Br, ^{81}Br). ^1H NMR ($CDCl_3$, 60 MHz): δ 7.0 (s, 2 H_b) and 3.8 (s, 6 H_d).

Compound **IIb**. Benzo-15-crown-5 (5 g, 0.019 mol) was dissolved in glacial acetic acid (10 cm^3) and bromine (2.02 cm^3, 0.038 mol) added as a solution in glacial acetic acid (10 cm^3). The bromine colour rapidly faded with concomitant evolution of heat and white fumes of HBr. After *ca.* 30 min (the exact time depended upon the amount of acetic acid used) a crystalline orange precipitate separated. The mixture was stirred at room temperature for several hours, to ensure complete reaction. The precipitate was filtered off and washed with a little cold glacial acetic acid. The excess of bromine was removed from the solid by treatment with acetone; this process was exothermic and HBr was evolved. The acetone was removed by evaporation at reduced pressure, leaving a pale brown syrup. The bromine could also be removed by shaking the orange CH_2Cl_2 solution of the initial precipitate with a saturated aqueous solution of $NaHSO_3$ and the product obtained by evaporation to dryness. The product thus obtained proved suitable for use in the next stage of the synthesis. However, the syrup could be crystallised from a cooled hexane solution to give a white solid. Yield *ca.* 90% (Found: C, 38.9; H, 4.2; Br, 37.0. $C_{14}H_{18}Br_2O_5$ requires C, 39.5; H, 4.3; Br, 37.5%); *m/z* (EI) 426 (5.6, M^+, ^{79}Br, ^{81}Br), (CI) 426 (100%, M^+). NMR [$(CD_3)_2CO$]: ^1H (300 MHz), δ 7.25 (s, 2 H_b), 4.16 (m, 4 H_d), 3.86 (m, 4 H_e) and 3.69 (m, 8 $H_{f,g}$); ^{13}C (75 MHz), δ 150.1 (C_c), 119.1 (C_b), 115.3 (C_a), 71.9 (C_d), 71.0 (C_e), 70.1 (C_f) and 70.0 (C_g).

Compound **IIIb**. Benzo-18-crown-6 (5.8 g, 0.019 mol) was dissolved in glacial acetic acid (20 cm^3) and bromine (6.08 g, 1.95 cm^3, 0.039 mol) in glacial acetic acid (20 cm^3) added slowly. The mixture was stirred overnight at room temperature. Water

(25 cm^3) was added and the aqueous layer then extracted with CH_2Cl_2 (3 × 25 cm^3) to give an orange-brown solution. This was washed with saturated, aqueous $NaHSO_3$ to remove the excess of bromine, leaving an essentially colourless solution which was dried over $MgSO_4$. This material was not purified further before subsequent use.

Compound **IVb**.[14] To a stirred slurry of dibenzo-18-crown-6 (1 g, 2.77 mmol) in glacial acetic acid (3 cm^3) was added bromine (0.6 cm^3, 11.1 mmol) in glacial acetic acid (5 cm^3). After 1 h dark orange crystals were obtained. The mixture was heated, under reflux, for 5 h to leave a white solid below a pale orange solution. The solid was filtered off and washed with glacial acetic acid and then acetone. The acetone reacted with any residual bromine giving fumes of HBr. Yield *ca.* 90% (Found: C, 35.2; H, 2.9; Br, 47.1. $C_{20}H_{20}Br_4O_6$ requires C, 35.5; H, 3.0; Br, 47.3%); *m/z* (EI) 676 (14.5, M^+, $^{79}Br_2$, $^{81}Br_2$), 596 (3.2, M^+ − Br) and 516 (1%, M^+ − 2Br). NMR ($CDCl_3$): ^1H (300 MHz), δ 7.03 (s, 4 H_b), 4.12 (m, 8 H_d) and 3.97 (m, 8 H_e); ^{13}C (75 MHz), δ 148.3 (C_c), 117.3 (C_b), 114.9 (C_a), 69.5 (C_d) and 68.8 (C_e)

1,2-*Bis*(n-*butylthio*)-4,5-*dimethoxybenzene* **Ic**. 4,5-Dibromoveratrole **Ib** (2 g, 6.33 mmol) and copper(I) butanethiolate (2.12 g, 0.014 mol) were heated, under reflux, in a mixture of quinoline (10 cm^3, freshly distilled from powdered zinc[38]) and pyridine (3 cm^3), with mechanical stirring. The reaction required a reflux time of 6–7 h, this having been established by following the reaction by TLC. During the reflux all the initially undissolved material dissolved to give a dark green solution. After completion of the reflux the mixture was allowed to cool to 100 °C then poured into ice–water (30 g) containing 12 mol dm^{-3} HCl (10 cm^3). This yielded a dark, gummy solid which was allowed to stand with occasional stirring for 2 h. The water was decanted and washed with diethyl ether (2 × 15 cm^3). The ether extract was then added to the gummy residue and stirred for 10 min. The gum was extracted a further four times with portions of ether (15 cm^3), until the extract was colourless. The red-brown ether solution was washed with portions of water (1 × 25 cm^3), hydrochloric acid (2 × 25 cm^3), water (1 × 25 cm^3), 15 mol dm^{-3} ammonia solution (2 × 25 cm^3) and, finally, water (2 × 25 cm^3). The ether layer was dried over $MgSO_4$ and the solvent evaporated to give a dark red oil. On standing the oil crystallised to give the product as large, transparent, crystalline blocks. The product was also purified by column chromatography on silica gel (Merck Kieselgel 60 H, Art. 7736) eluted with diethyl ether. Yield *ca.* 60%. M.p. 52–55 °C (Found: C, 61.1; H, 8.5; S, 20.7. $C_{16}H_{26}O_2S_2$ requires C, 61.1; H, 8.3; S, 20.4%); *m/z* (EI) 314 (100, M^+) and 258 (62.4%, M^+ − Bu^n). NMR ($CDCl_3$): ^1H (300 MHz), δ 6.9 (s, 2 H_b), 3.88 (s, 6 H_d), 2.86 (br, 4 H, $SCH_2CH_2CH_2CH_3$), 1.62 (m, 5 lines, 4 H, $SCH_2CH_2CH_2CH_3$), 1.45 (m, 6 lines, 4 H, $SCH_2CH_2CH_2CH_3$) and 0.92 (t, 6 H, $SCH_2CH_2CH_2CH_3$); ^{13}C (75 MHz), δ 147.8 (C_c), 129.2 (C_a), 114.3 (C_b), 56.1 (C_d), 34.3 ($SCH_2CH_2CH_2CH_3$), 31.2 ($SCH_2CH_2CH_2CH_3$), 22.1 ($SCH_2CH_2CH_2CH_3$) and 13.8 ($SCH_2CH_2CH_2CH_3$).

Compound **IIc**. Compound **IIb** (0.5 g, 1.17 mmol) and copper(I) butanethiolate (0.4 g, 2.36 mmol) were added to freshly distilled quinoline[38] (8 cm^3) and pyridine (2.4 cm^3). Upon warming, all the solids dissolved to give a dark green solution which was refluxed for 8 h; the course of the reaction was followed by TLC, diethyl ether with a few drops of MeOH being used as eluent. When the reaction was complete, a work-up procedure identical to that described for **Ic** was followed. The crude product was subjected to column chromatography on silica gel, eluted first with CH_2Cl_2 and then diethyl ether which removed several by-products. The product was washed from the column using diethyl ether–MeOH (10 : 1 v/v). The product was usually obtained as a dark red-brown oil which proved difficult to crystallise. This was eventually achieved from light petroleum (b.p. 40–60 °C). Yield *ca.* 60% (Found: C, 59.3; H, 8.5; S, 14.2. $C_{22}H_{36}O_5S_2$ requires C, 59.4; H, 8.2; S, 14.4%); *m/z* (EI) 444 (100%, M^+). NMR ($CDCl_3$): ^1H (60 MHz), δ 6.8 (s, 2 H_b), 3.6–4.4 (br, m, 16 $H_{d,e,f,g}$), 2.8 (br, t, 4 H, $SCH_2CH_2CH_2CH_3$), 1.5 (br, m, 8 H, $SCH_2CH_2CH_2CH_3$), 0.95 (br, m, 6 H, $SCH_2CH_2CH_2CH_3$).

Compound **IIIc**. Compound **IIIb** (5 g, 0.011 mol) and copper(I) butanethiolate (3.6 g, 0.024 mol) were heated together in a refluxing mixture of freshly distilled quinoline[38] (30 cm^3) and pyridine (10 cm^3), in the same manner as described for **Ic**. After a reaction time of 8 h, a work-up identical to that described for **Ic** was followed, yielding a dark oil which was not subjected to further purification. Yield *ca.* 60%. *m/z* (EI) 488 (100, M^+) and 400 (47.1%, M^+ − SBu). ^1H NMR ($CDCl_3$, 80 MHz): δ 6.8 (s, 2 H_b), 4.2–4.0 (m, 4 H_d), 4.0–3.8 (m, 4 H_e), 3.6 (d, 12 $H_{f,g,h}$), 2.9–2.6 (m, 4 H, $SCH_2CH_2CH_2CH_3$), 1.6–1.1 (m, 8 H, $SCH_2CH_2CH_2CH_3$) and 0.9–0.7 (m, 6 H, $SCH_2CH_2CH_2CH_3$).

Compound **IVc**. Compound **IVb** (1.25 g, 1.85 mmol) and copper(I) butanethiolate (1.24 g, 8.15 mmol) were added to quinoline (10 cm^3) and pyridine (3 cm^3), and the mixture heated, under reflux, for 24 h, with mechanical stirring. The product was isolated, in the manner already described for the other thioethers, as a dark oil. *m/z* (FAB) 712 (100, M^+) and 624 (75%, M^+ − SBu). ^1H NMR ($CDCl_3$, 80 MHz): δ 6.75 (s, 4 H_b), 4.2–3.8 (br, d, 16 $H_{d,e}$), 2.9–2.6 (m, 8 H, $SCH_2CH_2CH_2CH_3$), 1.7–1.1 (m, 16 H, $SCH_2CH_2CH_2CH_3$) and 1.0–0.6 (m, 12 H, $SCH_2CH_2CH_2CH_3$).

Dilithium 4,5-*dimethoxybenzene*-1,2-*dithiolate*, Li_2L^1. 1,2-Bis(*n*-butylthio)-4,5-dimethoxybenzene **Ic** (1 g, 3.2 mmol) was dissolved in a minimum quantity of dry tetrahydrofuran (thf), used as a cosolvent, and placed in a three-necked, round-bottom flask which had previously been flushed with dinitrogen. One neck of the flask was connected to the dinitrogen supply, one to an ammonia cylinder and the third to a bubbler through a solid CO_2–acetone condenser. A slow stream of ammonia gas was admitted to the reaction vessel until *ca.* 10 cm^3 of liquid ammonia had condensed. At this point the ammonia flow was stopped but a slow stream of dinitrogen was maintained for the duration of the experiment. Lithium metal (at least 3 equivalents) was added portionwise through the ammonia inlet, the blue colour being allowed to discharge between additions. When the blue colour of lithium in ammonia persisted, unabated, for over 30 min, the reaction was adjudged to be complete. An excess of solid NH_4Cl was then added to destroy the excess of lithium. The rate of flow of the dinitrogen gas was then increased and the liquid ammonia allowed to evaporate. The residual thf solvent was evaporated under reduced pressure to leave an off-white solid containing the required dilithium salt.

4,5-*Dimethoxybenzene*-1,2-*dithiol*, H_2L^1. The crude lithium salt **Id** was dissolved in an ice–water mixture and universal indicator paper used to check that the solution was alkaline. If it was not, a small quantity of 2 mol dm^{-3} NaOH was added. The aqueous solution was then washed with ether (2 × 20 cm^3) and acidified with 12 mol dm^{-3} HCl. At pH < 3 a pale green precipitate appeared which was immediately extracted into CH_2Cl_2 (2 × 25 cm^3) to give a green solution. The solution was degassed and dried over $MgSO_4$, under dinitrogen. Filtration, followed by evaporation of the solvent under reduced pressure, gave the crude dithiol, usually as a dark green oil. This product was used directly in the synthesis of transition-metal complexes. Attempts to purify the dithiol by column chromatography were unsuccessful. *m/z* (EI) 202 (100, M^+) and 170 (86.5%, M^+ − S). NMR ($CDCl_3$): ^1H (300 MHz), δ 6.83 (s, 2 H_b) and 3.75 (s, 6 H_d); ^{13}C (75 MHz), δ 148.0 (C_c), 122.0 (C_a), 114.2 (C_b) and 55.9 (C_d).

Dilithium salt **IId**. Typically, compound **IIc** (2 g, 4.5 mmol) was reduced with an excess of lithium metal, in liquid ammonia, in an identical procedure to that outlined for **Id**. The crude dithiolate salt was produced as an off-white solid which was used directly in the reaction described below to give H_2L^2.

2,3,5,6,8,9,11,12-*Octahydro*-1,4,7,10,13-*benzopentaoxacyclopentadecine*-15,16-*dithiol*, H_2L^2. The crude dilithium salt **IId** was dissolved in water and protonated with 12 mol dm^{-3} HCl in the manner described in the synthesis of H_2L^1. Extraction of the free dithiol into CH_2Cl_2 led to the isolation of a dark green oil which was used directly in the synthesis of transition-metal complexes. *m/z* (EI) 332 (27.5, M^+) and 300 (48.1%, $M^+ - S$). NMR ($CDCl_3$): ^1H (300 MHz), δ 6.9 (m, 2 H_b), 4.2–4.0 (br s, 4 H_d), 4.0–3.75 (br s, 4 H_e) and 3.75–3.6 (br s, 8 $H_{f,g}$); ^{13}C (75 MHz), δ 148.1 (C_c), 122.7 (C_a), 117.3 (C_b), 70.9 (C_d), 70.3 (C_e), 69.3 (C_f) and 69.2 (C_g).

Dilithium salt **IIId**. Typically the thioether **IIIc** (2–5 g) was reduced to the dithiolate salt using lithium metal in liquid ammonia under conditions identical to those described for **Id**. The impure salt was isolated as a pale brown solid.

2,3,5,6,8,9,11,12,14,15-*Decahydro*-1,4,7,10,13,16-*benzohexaoxacyclooctadecine*-18,19-*dithiol*, H_2L^3. The crude dilithium salt **IIId** was protonated, in water, with 12 mol dm^{-3} HCl. Extraction into CH_2Cl_2 led to the isolation of the impure, free dithiol as a dark oil which was used in the synthesis of several transition-metal complexes. *m/z* (EI) 376 (0.5, M^+) and 344 (71.8%, $M^+ - S$). ^1H NMR ($CDCl_3$ 80 MHz): δ 6.9–6.7 (br s, 2 H_b), 4.2–4.0 (br s, 4 H_d), 4.0–3.8 (br s, 4 H_e) and 3.8–3.6 (br d, 12 $H_{f,g,h}$).

$[MoL^1{}_3]$ **1**. Anhydrous $MoCl_5$ (0.37 g, 1.35 mmol) was dissolved in dried, redistilled CH_2Cl_2 (50 cm^3) and stirred, under dinitrogen, to give a dark red solution. To this was added a solution of veratroledithiol H_2L^1 (0.84 g, 4.16 mmol) in CH_2Cl_2 (5 cm^3). The reaction mixture rapidly became very dark and was stirred, at room temperature, for several hours. It was not necessary to heat the solution to reflux as in similar syntheses.[17] At this stage the reaction was handled in the atmosphere. The solvent was removed, at reduced pressure, to give an oily brown solid which was redissolved in dichloromethane (*ca.* 10 cm^3) and filtered. A red-green dichroic solid could be obtained at this stage by the gradual addition of pentane to the CH_2Cl_2 solution. This material was purified by column chromatography on silica gel (Merck Art. 7736 60 H), eluted with CH_2Cl_2, and successfully recrystallised from the same solvent, by layering with hexane. Yield *ca.* 50%.

$[MoL^2{}_3]$ **2**. Anhydrous $MoCl_5$ (0.14 g, 0.50 mmol) was dissolved in dry, redistilled CH_2Cl_2 (30 cm^3) and stirred, under dinitrogen, to give a red solution. To this solution was added H_2L^2 (0.5 g, 1.5 mmol) in CH_2Cl_2 (5 cm^3). The reaction was stirred at room temperature for several hours, rapidly becoming dark. The solution was filtered and the solvent was removed, at reduced pressure, until the total volume of the solution was *ca.* 10 cm^3. A brown solid was precipitated from the solution by the addition of pentane. This crude product was purified by column chromatography, on silica gel, eluting first with CH_2Cl_2. The characteristic red-brown band due to the product was eluted from the column using CH_2Cl_2–MeOH (10 : 1 v/v). Attempts to recrystallise the product from CH_2Cl_2 by layering with hexane gave only amorphous material. Yield *ca.* 50%.

$[MoL^3{}_3]$ **3**. Anhydrous $MoCl_5$ (0.12 g, 0.44 mmol) was dissolved, under dinitrogen, in dry, redistilled CH_2Cl_2 (25 cm^3) and H_2L^3 (0.5 g, 1.33 mmol) added as a solution in dichloromethane (5 cm^3). The resulting dark solution was stirred under dinitrogen for 8 h with no further change in its appearance. After this time the solvent was removed under reduced pressure and the resulting brown solid was dissolved in the minimum volume of CH_2Cl_2 and purified by chromatography on silica gel. The product was eluted from the column with CH_2Cl_2–MeOH (10 : 1 v/v). Yield *ca.* 30%.

$[WL^1{}_3]$ **4**. Anhydrous WCl_6 (0.37 g, 0.93 mmol) was dissolved, under dinitrogen, in dry, redistilled CH_2Cl_2 (25 cm^3) and treated with veratroledithiol H_2L^1 (0.57 g, 2.8 mmol) as a solution in CH_2Cl_2 (5 cm^3). The solution was stirred overnight under dinitrogen to give a green or, sometimes, purple solution. The solution was filtered and reduced in volume before being purified by chromatography on silica gel. The green product-containing band was eluted from the column with CH_2Cl_2. Yield *ca.* 40%.

$[WL^2{}_3]$ **5**. Anhydrous WCl_6 (0.16 g, 0.40 mmol) was added to dry CH_2Cl_2 (20 cm^3), under dinitrogen, to give a dark red slurry. To this was added H_2L^2 (0.42 g, 1.26 mmol) in a further small quantity of CH_2Cl_2. The reaction mixture was treated as for **4**, the product band being eluted from the column with CH_2Cl_2–MeOH (10 : 1 v/v). Yield *ca.* 50%.

$[NEt_4][NiL^1{}_2]$ **6**. Absolute ethanol (10 cm^3) was added to veratroledithiol H_2L^1 (0.48 g, 2.38 mmol), under dinitrogen. Potassium metal (0.19 g, 4.9 mmol) was added whereupon the dithiol began to dissolve giving an orange solution of the potassium salt. The salt $NiCl_2 \cdot 6H_2O$ (0.28 g, 1.18 mmol) was added, with stirring, as a solution in absolute ethanol (15 cm^3). The reaction mixture immediately developed an intense red-brown colouration and after 5 min $[NEt_4]Br$ (0.25 g, 1.19 mmol) was added as a solution in absolute ethanol (10 cm^3). After cooling at *ca* −5 °C, for about an hour, a green solid precipitated which was washed with cold ethanol and diethyl ether. The crude solid was recrystallised from CH_2Cl_2 layered with hexane, to give shiny green plates. Yield *ca.* 45%.

$[NiL^2{}_2]^-$ **7**. The route described for complex **6** was followed. Compound H_2L^2 (0.63 g, 1.90 mmol) in absolute ethanol (10 cm^3) was treated with potassium metal (0.15 g, 3.8 mmol), under dinitrogen. The salt $NiCl_2 \cdot 6H_2O$ (0.23 g, 0.97 mmol) was added producing a red-brown colour almost immediately. The addition of various quaternary ammonium and related cations (see text) did not lead to the precipitation of the required complex. Solid material was finally obtained by adding pentane to concentrated CH_2Cl_2 solutions of the crude material. The identity of the cation present in this solid product was not clear.

$[NiL^3{}_2]^-$ **8**. The procedure followed was the same as that described for anion **7**. A yellow-green solid was isolated which was not fully characterised.

$[NiL^1(dppe)]$ **9**. Veratroledithiol H_2L^1 (0.3 g, 1.49 mmol) was treated with sodium metal (0.07 g, 3.0 mmol) in MeOH (10 cm^3), with a few drops of CH_2Cl_2 being added after the addition of the sodium to enhance the solubility of the dithiol. An orange solution of $[Ni(dppe)Cl_2]$[20] (0.78 g, 1.48 mmol), in CH_2Cl_2 (40 cm^3), was added to the dithiolate solution, producing a dark red colour. After stirring this for 4 h at room temperature, a dark precipitate formed and the solution had a slight purple colour. The mixture was stirred overnight, filtered and pumped to dryness. The resulting solid was washed with acetone (2 × 20 cm^3), giving a brown solution and leaving a purple solid. The purple solid was dissolved in $CHCl_3$, giving a dark blue-purple dichroic solution which was washed with water (2 × 50 cm^3) and the $CHCl_3$ layer dried over $MgSO_4$. Removal of the solvent, at reduced pressure, gave a purple crystalline solid which was recrystallised from CH_2Cl_2 layered with hexane to produce shiny purple needles. Yield *ca.* 60%.

$[NiL^2(dppe)]$ **10**. Compound H_2L^2 (0.5 g, 1.50 mmol) was treated with potassium metal (0.12 g, 3.1 mmol), under dinitrogen, in methanol (10 cm^3). The complex $[Ni(dppe)Cl_2]$[20] (0.78 g, 1.48 mmol) was added as a solution in CH_2Cl_2 (50 cm^3). The reaction proceeded in the same way as described for **9** and the product isolated in an identical manner to give a similarly dichroic blue-purple solution in $CHCl_3$. This solution was evaporated to dryness and the crude solid purified by column chromatography on silica gel. The product was eluted from the column with CH_2Cl_2–MeOH (10 : 1 v/v). Recrystallisation from CH_2Cl_2, by cooling a solution to which a small quantity of hexane had been added, produced purple needles. Yield *ca.* 70%.

$[NiL^3(dppe)]$ **11**. This compound was prepared in exactly the manner described for **10**. The only difference was that complex **11** could not be successfully recrystallised. Yield *ca.* 75%.

$[CoL^1(\eta^5\text{-}C_5H_5)]$ **12**. Veratroledithiol H_2L^1 (0.75 g, 3.7 mmol) was deprotonated by reaction with potassium metal (0.30 g, 7.5 mmol) in MeOH (10 cm^3). To this was added $[Co(\eta^5\text{-}C_5H_5)(CO)I_2]$[39] (1.5 g, 3.7 mmol), dissolved in CH_2Cl_2 (40 cm^3). An immediate deep blue solution resulted which was stirred under dinitrogen for 1 h. The solution was filtered, washed with water (3 × 50 cm^3), dried over $MgSO_4$, concentrated and an attempt made to purify it by column chromatography on silica gel with CH_2Cl_2–MeOH elution. The blue product was successfully recrystallised as a shiny blue-purple solid. Yield *ca.* 40%.

[CoL^2(η^5-C_5H_5)] **13**. Compound H_2L^2 (0.4 g, 1.2 mmol) was added to potassium metal (0.1 g, 2.5 mmol) in MeOH (10 cm^3); CH_2Cl_2 (10 cm^3) was added to enhance the solubility of the dithiol. A solution of [Co(η^5-C_5H_5)(CO)I_2][39] (0.49 g, 1.2 mmol) in CH_2Cl_2 (20 cm^3) was added, leading to the instantaneous formation of a deep blue solution. This was stirred under dinitrogen for 1 h. The reaction mixture was worked up in a manner similar to that described for **12**. No success was achieved in attempts to crystallise the material. Yield *ca.* 35%.

[CoL^3(η^5-C_5H_5)] **14**. This compound was synthesised in a manner analogous, at all stages, to that described for **13**. The material could not be purified satisfactorily and was obtained as a sticky, blue solid.

[TiL^1(η^5-C_5H_5)$_2$] **15**. Veratroledithiol H_2L^1 (0.5 g, 2.48 mmol) and [Ti(η^5-C_5H_5)$_2Cl_2$] (0.61 g, 2.48 mmol) were dissolved in CH_2Cl_2 (40 cm^3) giving a dark red solution. As soon as a few drops of NEt_3 were added to the stirred solution a bottle-green colour developed. The solution was filtered and reduced in volume prior to column chromatography on silica gel. The column was eluted, first with CH_2Cl_2 and then the blue-green product band washed from the column with CH_2Cl_2–ethyl acetate (20:1 v/v). After removal of the solvent a shiny, dark green solid was obtained. Attempts were made to crystallise this material from several solvent systems but only amorphous material was obtained. Yield *ca.* 80%.

[TiL^2(η^5-C_5H_5)$_2$] **16**. This compound was made in the same way as **15**, from equimolar quantities of H_2L^2 and [Ti(η^5-C_5H_5)$_2Cl_2$], mixed in CH_2Cl_2, in the presence of a few drops of NEt_3. Typically, 0.5 g of the dithiol was used in *ca.* 40 cm^3 of solvent. Attempts were made to purify the crude product by column chromatography on silica gel. The bottle-green product was eluted with CH_2Cl_2–MeOH (10:1 v/v). The product was obtained as a dark green powder. Yield *ca.* 80%.

[TiL^3(η^5-C_5H_5)$_2$] **17**. This compound was synthesised in the manner described for **16** and isolated as a dark green solid. Yield *ca.* 50%.

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References

1 R. E. Wolf, jun. and S. R. Cooper, *J. Am. Chem. Soc.*, 1984, **106**, 4646; A. Kaifer, L. Echegoyen, D. A. Gustowski, D. M. Goli and G. W. Gokel, *J. Am. Chem. Soc.*, 1983, **105**, 7168; A. Kaifer, D. A. Gustowski, L. Echegoyen, V. J. Gatto, R. A. Schultz, T. P. Cleary, C. R. Morgan, D. M. Goli, A. M. Rios and G. W. Gokel, *J. Am. Chem. Soc.*, 1985, **107**, 1958; L. Echegoyen, D. A. Gustowski, V. J. Gatto and G. W. Gokel, *J. Chem. Soc., Chem. Commun.*, 1986, 220; T. Saji, *Chem. Lett.*, 1986, 275; C. D. Hall, N. W. Sharpe, I. P. Danks and Y. P. Sang, *J. Chem. Soc., Chem. Commun.*, 1989, 419; P. D. Beer, H. Sikanyika, J. F. McAleer and M. G. B. Drew, *J. Organomet. Chem.*, 1988, **356**, C19; N. A. Obaidi, P. D. Beer, J. P. Bright, C. J. Jones, J. A. McCleverty and S. S. Salam, *J. Chem. Soc., Chem. Commun.*, 1986, 239; E. Fu, M. L. H. Green, V. J. Lowe and S. R. Marder, *J. Organomet. Chem.*, 1988, **341**, C39; E. Fu, J. Granell, M. L. H. Green, V. J. Lowe, S. R. Marder, G. C. Saunders and M. Tuddenham, *J. Organomet. Chem.*, 1988, **355**, 205.

2 H. Nakamura, H. Sakka, M. Takagi and K. Ueno, *Chem. Lett.*, 1981, 1305; H. Nishida, Y. Katayama, H. Katsuki, H. Nakamura, M. Takagi and K. Ueno, *Chem. Lett.*, 1982, 1853; N. Kobayashi and Y. Nishiyama, *J. Chem. Soc., Chem. Commun.*, 1986, 1462.

3 M. Shiga, M. Takagi and K. Ueno, *Chem. Lett.*, 1980, 1021; A. Hrieiga and J. M. Lehn, *Proc. Natl. Acad. Sci. USA*, 1983, **80**, 6426.

4 J. Rebek, jun., R. V. Wattley, T. Costello, R. Gradwood and L. Marshall, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 605; P. D. Beer, *J. Chem. Soc., Chem. Commun.*, 1986, 1678; M. L. H. Green, S. R. Marder, G. C. Saunders and N. M. Walker, *J. Chem. Soc., Dalton Trans.*, 1988, 1697; J. Granell, M. L. H. Green, V. J. Lowe, S. R. Marder, P. Mountford, G. C. Saunders and N. M. Walker, *J. Chem. Soc., Dalton Trans.*, 1990, 605.

5 P. D. Beer, *Chem. Soc. Rev.*, 1989, **18**, 409 and refs. therein.

6 See, for example, C. D. Hall, N. W. Sharpe, I. P. Danks and Y. P. Sang, *J. Chem. Soc., Chem. Commun.*, 1989, 419.

7 M. P. Andrews, C. Blackburn, J. F. McAleer and V. D. Patel, *J. Chem. Soc., Chem. Commun.*, 1987, 1122.

8 M. L. H. Green, W. B. Heuer and G. C. Saunders, *J. Chem. Soc., Dalton Trans.*, 1990, 3789.

9 N. D. Lowe, Ph.D. Thesis, University of Manchester, 1990.

10 N. D. Lowe and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, submitted.

11 R. Adams, W. Reifschneider and A. Ferretti, *Org. Synth.*, 1962, **42**, 22.

12 A. Ferretti, *Org. Synth.*, 1962, **42**, 54.

13 M. Kohn, *J. Am. Chem. Soc.*, 1951, **73**, 480.

14 E. Shchori and J. Jagur-Grodzinski, *Isr. J. Chem.*, 1972, **10**, 935.

15 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 49.

16 R. Eisenberg, *Prog. Inorg. Chem.*, 1970, **12**, 295; R. P. Burns and C. A. McAuliffe, *Adv. Inorg. Chem. Radiochem.*, 1979, **22**, 303.

17 E. I. Stiefel, R. Eisenberg, R. C. Rosenberg and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 2956.

18 W. Clegg, personal communication, 1987.

19 R. Williams, E. Billig, J. H. Waters and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 43.

20 G. R. van Hecke and W. DeW. Horrocks, jun., *Inorg. Chem.*, 1966, **5**, 1968.

21 R. F. Heck, *Inorg. Chem.*, 1968, **7**, 1513.

22 M. Bottrill, P. D. Gavens, J. W. Kelland and J. McMeeking, in *Comprehensive Organometallic Chemistry*, eds. G. Wilkinson, F. G. A. Stone and E. W. Abel, Pergamon, Oxford, 1982, vol. 3, pp. 384–391.

23 E. I. Stiefel and H. B. Gray, *J. Am. Chem. Soc.*, 1965, **87**, 4012.

24 G. N. Schrauzer and V. P. Mayweg, *J. Am. Chem. Soc.*, 1966, **88**, 3235.

25 S. Boyde, C. D. Garner, J. A. Joule and D. J. Rowe, *J. Chem. Soc., Chem. Commun.*, 1987, 800.

26 G. A. Bowmaker, P. D. W. Boyd and G. K. Campbell, *Inorg. Chem.*, 1982, **21**, 2403.

27 R. B. King and C. A. Eggers, *Inorg. Chem.*, 1968, **7**, 340.

28 J. A. McCleverty, *Prog. Inorg. Chem.*, 1968, **10**, 122–125.

29 H. Köpf, *Angew. Chem.*, 1971, **83**, 146; H. Köpf and T. Klapötke, *Z. Naturforsch., Teil B*, 1986, **41**, 667.

30 H. Eyring, *Chem. Rev.*, 1935, **17**, 65.

31 D. Kost, E. H. Carlson and M. Raban, *Chem. Commun.*, 1971, 656.

32 M. J. Baker-Hawkes, E. Billig and H. B. Gray, *J. Am. Chem. Soc.*, 1966, **88**, 4870.

33 E. M. Armstrong, personal communication, 1989.

34 A. Davison, N. Edelstain, R. H. Holm and A. H. Maki, *Inorg. Chem.*, 1964, **3**, 814.

35 R. Greef, R. Peat, L. M. Peter, D. Pletcher and J. Robinson, Southampton Electrochemistry Group, Ellis Horwood, Chichester, 1985, *Instrumental Methods in Electrochemistry*, ch. 6.

36 M. Kajitani, T. Akiyama, A. Sugimori, K. Hirakata, Y. Hoshino, Y. Satsu, G. P. Sato, K. Shimizu, M. Kaise and C. Nishihara, *J. Electroanal. Chem. Interfacial Electrochem.*, 1988, **251**, 421.

37 C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.

38 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd edn., Pergamon, Oxford, 1980, p. 407.

39 R. F. Heck, *Inorg. Chem.*, 1965, **4**, 855.

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